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Transition in clay till settings

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DTU Environment
Department of Environmental Engineering

PhD Thesis
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Preface

This thesis comprises the research carried out for a PhD project undertaken from 2009 to 2012 at DTU Environment, Technical University of Denmark. The thesis was funded by the GOODWATER project of European Commission's Marie Curie Initial Training Network for young scientists under grant no. 212683. The study included an external research visit at the IGÖ Institute for Groundwater Ecology at Helmholz Zentrum Munich during September and October 2011. The primary supervisor was Professor Poul L. Bjerg, the co-supervisor was Professor Hans-Jørgen Albrechtsen and the supervisor during the external research visit was Dr. Martin Elsner.

The PhD thesis comprises a synopsis of the work presented in one accepted paper, one submitted paper and two manuscripts in preparation. In the synopsis of the thesis the papers are referred to by the names of the authors and the Roman numerals I-IV (e.g. Milosevic et al., **II**). The papers included in the thesis are:

I Thomsen, N.I., Milosevic, N. and Bjerg, P.L., 2012. Application of a mass balance method at an old landfill to assess the impact on surrounding water resources, submitted manuscript

II Milosevic, N., Thomsen, N.I., R.K. Juhler, Albrechtsen, H.-J. and Bjerg, P.L., 2012. Identification of discharge zones and quantification of contaminant fluxes into a local stream from a landfill in heterogeneous geological settings, Journal of Hydrology, DOI 10.1016/j.jhydrol.2012.04.012, in press.

III Milosevic, N., Qiu, S., Elsner, M., Einsiedl, F., Albrechtsen, H.-J. and Bjerg, P.L., 2012. Combined isotope and enantiomer analysis to assess the fate of phenoxy acids in a heterogeneous geologic setting at an old landfill, manuscript in preparation

IV Batioglu-Pazarbasi, M., Milosevic, N., Malaguerra, F., Binning, P.J., Albrechtsen, H.-J., Bjerg, P.L. and Aamand, J., 2012. Discharge of landfill leachate to streambed sediments impacts the mineralization potential of phenoxy acid herbicides depending on the *tfdA* gene diversity, manuscript in preparation

The papers are not included in this web-version, but can be obtained from the Library at DTU Environment. Contact library@env.dtu.dk or Department of Environmental Engineering, Technical University of Denmark, Miljoevej, Building 113, DK-2800 Kgs. Lyngby, Denmark.

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Nemanja Milosevic

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I would like to thank my supervisors Professors Poul L. Bjerg and Hans-Jørgen Albrechtsen for their inspiring and professional guidance throughout my PhD study. I am grateful for the chance to learn in a structured scientific way.

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My co-authors and technicians from DTU Environment and Geological Survey of Denmark and Greenland are greatly acknowledged for a fruitful collaboration in paper writing, field and laboratory work.

A huge hug goes to my friends Davide, Karolina, Roberto, Fabrizio, Ana, Suzi and Erkin.

Very special thanks to Dijana and all my family for their unconditioned encouragement. Finally, I dedicate my scientific work to my mother, who taught me to think critically.

Abstract

Numerous landfill sites worldwide have been recognized as a threat to clean water resources. Many environmental legal acts have been issued and improved to tackle this problem. The main concern is caused by slow degradation of the disposed waste and the high complexity of field conditions (landfill history, geology and hydrogeology), which together result in a virtually unique setting at each landfill site. Nevertheless, many general principles derived from research sites and case studies in homogeneous geological settings can be applied or adjusted to fit specific, complex landfill cases.

Transition zones between different environmental conditions or between groundwater and surface water are regarded as places of high potential for contaminant attenuation. Special attention is given to the groundwater-surface water transition (hyporheic) zone, with a perspective that it can harbour particular microbial communities that can degrade even recalcitrant landfill-originating xenobiotic compounds.

The overall scope of the study was to deepen knowledge about the degradation of xenobiotic organic compounds in landfill leachate contaminated groundwater and in the transition from groundwater to surface water and to improve concepts, tools and methods for the degradation assessment.

High complexity in the field is challenging, since it influences the spreading of contamination and attenuation processes such as sorption and degradation. Clay till, a glacial deposit of low permeable clay with interbedded sand lenses, is a common soil type in Scandinavia and parts of North America. Therefore, a study site, the Risby Landfill west of Copenhagen, was chosen, since it encloses all key features for the research – an old landfill without leachate collection and liner, clay till-dominated geology and a local stream in the vicinity of the landfill.

The degradation was assessed for three xenobiotic groups detected in the Risby Landfill leachate: phenoxy acid pestidicides, chlorinated solvents and monoaromatic petroleum derivatives. The degradation assessment was based on a conceptual site model, using established lines of evidence of natural attenuation. The conceptual model was formulated for hydrogeology and water chemistry, providing water flow balance and mass discharges of selected contaminants. The model was improved by analyzing *in situ* indicators of

biodegradation, some of which were applied for the first time to landfill leachate contaminated groundwater in a clay till.

Natural attenuation of phenoxy acids was estimated to be significant in an area with very high concentrations of leachate indicators beneath the landfill (hotspot), along the groundwater flow towards the stream and in the hyporheic zone, using isotope, enantiomer and metabolite analyses. Phenoxy acids reached the Risby Stream, exerting local and small chemical impact. Nevertheless, the impact was seasonally very high in the periods of low stream flow. Chlorinated solvents and petroleum derivatives were detected only in the hotspot, and tracking of their fate along the groundwater flow direction was therefore not possible. Literature data on their isotope fractionation and degradation rates were used for the degradation assessment instead. Reductive dechlorination of chlorinated ethenes in the hotspot was shown, and back-release of the mother compound was indicated. Degradation of petroleum derivatives was also indicated in the hotspot. These findings on anaerobic degradation in the hotspot supported the indications of phenoxy acid degradation by reductive dechlorination.

A microbial study was conducted only for the aerobic part of the contaminant pathway. Degradation of phenoxy acids was studied in the aerobic streambed sediment, confirming high degradation potential in the hyporheic zone indicated earlier by indirect methods.

The field settings' complexity influenced the choice of methods. Compound-specific isotope analysis was applied for all groups of xenobiotic landfill leachate compounds, and its performance was evaluated with respect to its complementary usage with enantiomer and metabolite analyses. Isotope-based analysis without supportive microbial study sufficed for the qualitative assessment of degradation or for discrimination between different hotspots. Fractionation rates from literature or high fractionation along the groundwater flow would further improve the degradation assessment of the xenobiotic compounds to the quantification level.

Degradation of xenobiotic organic compounds in landfill contaminated groundwater was shown using multiple methods and multiple compound approaches. Concepts, tools and methods used for the degradation assessment were applied in a clay till setting with groundwater discharge into a local stream.

Dansk sammenfatning

Et stort antal lossepladser er på verdensplan blevet erkendt som en trussel mod vandkvaliteten. Miljølovgivning er løbende blevet udviklet og forbedret for at tackle dette problem. Den største bekymring er relateret til persistens af det deponerede affald og komplekse feltforhold (lossepladsens historik, geologi og hydrogeologi), som samlet set resulterer i en helt unik situation på hver lokalitet.

Alligevel kan mange principper udviklet fra undersøgelser af lossepladser under mere homogene geologiske forhold anvendes eller tilpasses mere komplekse forhold. Overgangszoner mellem forskellige miljøer eller mellem grundvand og overfladevand anses for at være områder med et betydeligt potentiale for nedbrydning af forureningsstoffer. Der er særlig opmærksomhed på overgangszonen mellem grundvand og overfladevand (hyporheiske zone), da den kan rumme specielle mikrobielle samfund, der kan nedbryde selv persistente organiske stoffer fra lossepladsen.

Projektets overordnede formål var at opnå en større viden om nedbrydning af miljøfremmede organiske stoffer i lossepladsforurenet grundvand og i overgangen mellem grundvand samt overfladevand og at forbedre koncepter, værktøjer og metoder for vurdering af nedbrydning.

En høj grad af kompleksitet på lokaliteten er udfordrende, da den påvirker spredning af forurening og attenueringsprocesser såsom sorption og nedbrydning. Moræneler, en glacial aflejring a lavpermeabel ler med indlejrede sandlinser, er almindelig i Skandinavien og Nordamerika. På den baggrund blev en feltlokalitet, Risby Losseplads, udvalgt, da den indeholder alle nøgleelementer for problemstillingen – en gammel losseplads uden perkolatopsamlingssystem eller membran, morænelersgeologi og kort afstand fra lossepladsen til et lokalt vandløb.

Nedbrydningen blev undersøgt for tre grupper af miljøfremmede stoffer fundet i Risby losseplads: phenoxysyrer pesticider, chlorerede opløsningsmidler og monoaromatiske benzinstoffer. Vurderingen af nedbrydningen var baseret på en konceptuel model for lokaliteten baseret på “lines of evidence” for naturlig nedbrydning. Den konceptuelle model blev formuleret for hydrogeologi og vandkemi, hvorved der blev etableret en vandbalance og stofflux for udvalgte stoffer. Modellen blev forbedret med analyser for *in situ* indikatorer, hvoraf nogle ikke tidligere er anvendt for lossepladsforurenet grundvand i moræneler.

Attenueringen af phenoxysyrer var på baggrund af analyser af isotoper, enantiomerer og metaboliter betydelig i et område med meget høje koncentrationer (”hotspot”) under lossepladsen, langs grundvandsstrømningen mod åen og i den hyporheiske zone. Phenoxysyrerne nåede Risby Å, hvor de foranledigede en mindre lokal kemisk påvirkning af åen. Der var dog i perioder med lille strømning i åen en betydelig påvirkning. Chlorerede opløsningsmidler og benzinstoffer blev kun fundet i ”hotspottet”, så deres skæbne kunne ikke følges i strømningsretningen. Litteraturdata blev i stedet brugt til at vurdere deres isotopfraktionering og nedbrydning. Reduktiv dechlorering af chlorerede ethener blev påvist og tilførsel af det oprindelige moderstof blev indikeret. Nedbrydning af benzinstoffer blev også indikeret i “hotspot”. Disse observationer om anaerob nedbrydning styrkede indikationerne for, at phenoxysyrer kunne blive nedbrudt ved reduktiv dechlorering.

Et mikrobielt studium blev gennemført for at belyse den aerobe nedbrydningsvej. Nedbrydning af phenoxysyrer blev studeret i det aerobe bundsediment i vandløbet. Resultaterne bekræftede et stort nedbrydningspotentiale i den hyporheiske zone, hvilket bekræftede tidligere indikationer.

Kompleksiteten af lokaliteten influerede på valg af metoder. Stabile isotopanalyser blev valgt for alle grupper af miljøfremmede stoffer, og dens muligheder som komplementær til enatiomer- og metabolitanalyser blev vurderet. Isotopanalyser uden hjælp fra mikrobielle studier var tilstrækkelig for en kvalitativ vurdering af nedbrydning eller for at skelne mellem forskellige ”hotspots”. Fraktioneringsdata fra litteraturen eller høj fraktionering langs strømningsretningen ville forbedre den kvantitative vurdering af nedbrydningen af de miljøfremmede stoffer.

Nedbrydning af miljøfremmede organiske stoffer i lossepladsperkolatforurenet grundvand blev påvist ved integreret anvendelse af flere metoder for forskellige stoffer. Koncepter, værktøjer og metoder er i dette studium blevet anvendt til vurdering af nedbrydning i moræneler i et område med grundvandsstrømning til et lokalt vandløb.

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1. Introduction

1.1 Background

Global scarcity of clean ground- and surface water is recognized by the environmental legislation bodies, but their acts for water protection are challenged by numerous emerging contaminants, complexity of contamination settings and several well-known recalcitrant contaminants. EU Water Framework Directive was issued in 2000 in a holistic way, encompassing all water compartments with a purpose to standardize them (European Commission, 2000). Its goal for year 2015 was for all water bodies to reach "good" environmental status. For the first time different water bodies were regarded in the legislation as an integrated water system. Special attention was given to transition zones and processes within them. Transition zone between shallow groundwater and surface waters was established in ecology as "the hyporheic zone" in the 50's and identified as a unique biotope in many aquatic ecosystems (Robertson and Wood, 2010). This zone is also a place of high microbial activity due to steep chemical gradients between anaerobic groundwater and aerobic surface water (e.g. Yu et al., 2010). As a place of attenuation of organic carbon, the groundwater transition zone influences the chemical and ecological status of the surface water (Smith and Lerner, 2008). Therefore, research focus is on the processes between different water compartments, with a perspective of the transition zone as a biological filter for attenuation of recalcitrant contaminants.

1.2 Landfills as a threat to clean water resources

Landfills in developed countries used to be formed by simple waste deposition without protection measures until a few decades ago, but unfortunately, that is still the case in many developing countries (Schwarzenbach et al., 2010). Waste deposition typically occurred on low-elevation places, where the flow path for their leachate to reach the groundwater is shorter and globally a large majority of landfills are groundwater-contaminating (Lambou et al., 1989; Lorah et al., 2009). There are at least 90,000 old landfills in the USA (Cozzarelli et al., 2011) and there are approximately 675,000 sites across Europe containing municipal and industrial waste (EEA, 2007), where a significant part of these are landfill sites. In Denmark alone more than 2,000 old landfills without leachate collection or liners have been mapped (Danish EPA, 2010). Old landfills are identified as an important pollution source that causes rather local but long-term deteriorating effect on the surrounding waters. In cases of groundwater-gaining surface waters, leachate can eventually reach local surface water at groundwater discharge zones.

Depending on geological settings and hydraulic potentials, such discharge zones can occur anywhere from headwaters to seas. However, their locations are most probable on low elevated terrains with high groundwater hydraulic heads, where old landfills are typical. Discharge of leachate-affected groundwater into stream has been proven on sites with low elevation (e.g. Yusof et al., 2009) but the exact places of discharge mostly remained unidentified and the deteriorating potential on chemical status of the stream water stayed uncertain.

1.3 Landfills as long-term point-sources of pollution

The chemical composition of the hotspot of pollution (area with very high concentrations of leachate indicators within the landfill) is a big unknown in estimation of chemical impact from landfills to the surrounding waters. Numerous landfill sites with poorly characterized and heterogeneous waste all over the world contain not only typical inorganic and organic contaminants but also xenobiotic compounds (Christensen et al., 2001) since products of chemical industry were widely available until the landfills' formation. Pesticides are common xenobiotic compounds in old landfills (Baun et al., 2004) since their usage has augmented during the last century's growth of population and the subsequent food production. Compared to the usual investigations of diffuse contamination from agricultural practice, not much attention has been paid on point-sources of pesticide pollution in the more recent studies (Bjerg et al., 2011). Aromatic hydrocarbons and chlorinated solvents are also well known xenobiotic compounds in landfills (Christensen et al., 2001; Kjeldsen et al., 2002), as they were commonly discarded as used petrol derivatives and chlorinated solvents.

Phenoxy acids are recalcitrant in strongly reduced landfill leachate (Buss et al., 2006; Harrison et al., 1998; Reitzel et al., 2004) but their degradation can be expected at nitrate-reducing or aerobic conditions (Harrison et al., 2003; Tuxen et al., 2006; Williams et al., 2003). Phenoxy acids pesticides are biologically active compounds. Their high mobility and recalcitrance in the anaerobic subsurface puts them on the list of chemicals that pose a risk for human health and deteriorate water resources (Buss et al., 2006).

Chlorinated solvents generally degrade under various anaerobic redox conditions, from methanogenic to nitrate reducing. They mainly follow a reductive dechlorination pathway where they act as electron donors, releasing chlorine atoms (Aeppli et al., 2010). Their attenuation in the core of a landfill leachate

plume can be high due to different redox conditions between the methanogenic landfill body and the more aerobic recipient water body (Bjerg et al., 2011). However, the degradation observed in the field is not always complete. Chlorinated solvents sequentially lose their chlorine atoms in the dechlorination process and the solvents with a lower number of chlorine atoms are expected to be bottlenecks of the sequential reaction (Nijenhuis et al., 2007). It results in their further migration to the aerobic environment and potential degradation by microbial oxidation, but such data have not been published from landfill leachate plumes to date (Bjerg et al., 2011).

BTEX compounds are petroleum derivatives and the most prominent group of aromatic pollutants detected in landfill leachate, with benzene as probably the most recalcitrant among them (Bjerg et al., 2011). Their degradation in aerobic conditions has been well studied and reviewed several times (e.g. Smith, 1990). However, hey are generally recalcitrant in anaerobic conditions since the available energy for breaking the benzene ring is not high. Nevertheless, their biodegradation by microorganisms, for which BTEX can be the only carbon source, is possible (Weelink et al., 2010).

1.4 Heterogeneity at landfill sites

A further challenge in investigation of landfills is intrinsic heterogeneity of both waste and underlying geologic settings, due to which landfill leachate cannot be predicted in detail except for predominant inorganic species. Spatial heterogeneity of the deposited waste is reflected as horizontal variability of leachate indicators in groundwater samples collected below the waste (Kjeldsen and Christophersen, 2001) and as both horizontal and vertical variability of the samples collected in complex geologic settings downgradient of the hotspot. Clay till is a common geologic formation in temperate and cold climates, with heterogeneous low-permeability matrix and high-permeability interbedded sandy strips and lenses (Gerber et al., 2001; Hendry et al., 2004; Klint and Gravesen, 1999; McKay et al., 1999; Nilsson et al., 2001). There have not been many field studies in such heterogeneous geological settings compared to studies in homogeneous sandy/gravel aquifers, due to technical complexity and high costs (Christensen et al., 2001). However, many concepts, tools and technologies for e.g. hydrogeology, contaminant transport and contaminant degradation have been developed for clay till settings (e.g. Chambon et al., 2011; Damgaard, 2012; Klint and Gravesen, 1999; McKay et al., 1999) and they can be applied in the field study procedures.

1.5 Objectives

The overall objective of the study was to assess the attenuation processes of landfill leachate contaminants in their transition through different parts of a landfill site with clay till settings. In addition, the objective was to improve concepts, tools and technologies for the investigation of ground- and surface water quality at such sites.

Specific objectives related to the heterogeneity of the confined leachate pathways in clay till was to apply multiple state-of-the-art methods for 1) identification of the groundwater-surface water transition zones at a landfill site, 2) quantification of groundwater discharge into a local stream in different scales and 3) estimation of chemical impact (contaminant mass discharge) of key leachate contaminants on the stream.

A specific objective for the selected xenobiotic organic compounds (phenoxy acids, chlorinated solvents and BTEX) was to assess their abiotic and biotic attenuation in the landfill leachate in different environmental conditions from the hotspot to the local stream. An additional objective was to evaluate the methods used for fate assessment of phenoxy acids.

Finally the study aim was to estimate the role of the groundwater-surface water transition zone as a biological filter for attenuation of landfill leachate-originating contaminants entering the stream.

Paper **I** dealt with overall mass balance at the landfill-scale and was the basis for the following, more specific mass discharge estimations. Paper **II** dealt with mass discharge on the scale of zones where groundwater discharges into the local stream. Paper **III** addresses the fate of organic leachate contaminants in different redox conditions along the confined groundwater flow path. Paper **IV** was a study on microbial potential for aerobic attenuation of phenoxy acid pesticides at the identified groundwater discharge zones.

1.6 Structure of the thesis

The structure of the thesis is as follows. Chapter 2 gives an overview of the strategy for making a conceptual site model, which is a base for the fate assessment. The choice of state-of-the-art fate assessment methods is presented in the context of complexity of contaminant chemistry and geological settings.

Formulation of the conceptual model includes findings on whole-site-scale hydrogeology, water chemistry and water discharge studied by Thomsen et al. (**I**) and a local-scale quantification of chemical discharge by Milosevic et al. (**II**). Chapter 3 includes improvements of these quantifications by deepening the understanding of the contaminant degradation, elaborating on the findings by Milosevic et al. (**III**). Findings by Batioglu-Pazarbasi et al. (**IV**) add to the microbial role in the degradation of phenoxy acids. Special attention is given to the novel application of the fate assessment methods for phenoxy acids. Thus, the contribution of the complementing methods was separately evaluated. Chapter 4 concludes the results of the thesis and the further research perspectives are discussed in Chapter 5.

2. Methods for assessment of natural attenuation of landfill leachate in clay till

Lines of evidence for the demonstration of natural attenuation of xenobiotic compounds at landfill sites and appropriate methods related to each line of evidence are issued in the U.S. EPA (1999) directive (Table 1). Evidences of *in situ* degradation build up a conceptual site model in three consecutive steps, using hydrogeologic, chemical and microbial methods. Computer modelling of the conceptual model is used as a supporting tool for integration of e.g. hydrogeological and chemical data (National Research Council, 2000). This chapter is subdivided according to the three steps of the model building.

A reliable assessment of natural attenuation of chemical mixtures requires usage of multiple methods, due to their long persistence as landfill contaminants. Usage of complementary hydrogeologic, chemical, microbial and molecular methods is recommended for comprehensive fate assessment studies in the field, but no universal technique exists so far. Related activities to each method are assigned to the papers in this study in Table 1.

Table 1: Toolbox with steps in making a conceptual landfill site model using lines of evidence for demonstration of natural attenuation and relevant methods; modified after U.S. EPA (1999) with related papers from this study and additional review references for the methods used in each step.

Line of evidence	Methods	This study
Step 1: Formulation of a conceptual model of the landfill site		
Developing of an initial site conceptual model	Analysis of geology, hydrology and water chemistry [α]	**I, II**
Documenting of contaminant mass loss in the field	Quantification of contaminant mass budget and discharge [β]	**I, II**
Step 2: Improvement of the conceptual site model		
Showing indicators of biodegradation in the field	Assessment of contaminant fate *in situ* [γ]	**III**
Step 3: Finishing of the conceptual site model		
Showing degradation potential	Microbial studies [δ]	**IV**

Review references
[α] Bjerg et al., 2011; Christensen et al., 2001; Cozzarelli et al., 2011
[β] Illman and Alvarez, 2009; National Research Council, 2000
[γ] Bjerg et al., 2011; Bombach et al., 2010; Elsner, 2010; Hofstetter and Berg, 2011; National Research Council, 2000; Reitzel, 2005
[δ] Bombach et al., 2010; Weiss and Cozzarelli, 2008

2.1 Formulation of a landfill site conceptual model

A conceptual model should formulate and identify the governing processes at the site and identify where the processes occur (Bjerg et al., 2011). As a first step, the initial conceptual model of the landfill site is formulated, in terms of hydrogeology, redox conditions and chemical parameters. This represents the basis for data evaluation, decision making in field and further iterative improvements of the model (Figure 1).

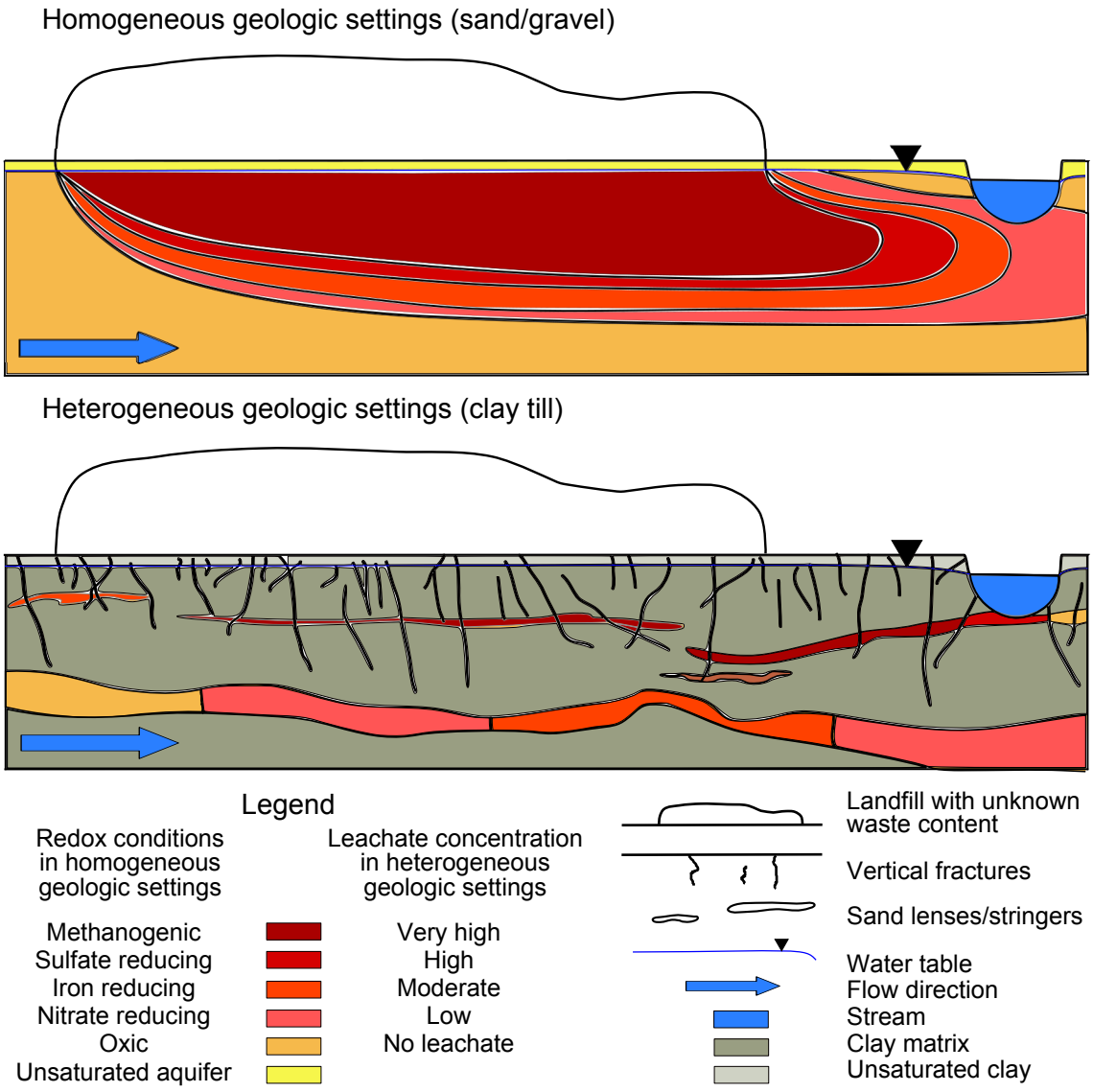

Figure 1: In case of a groundwater-gaining stream, conceptual models of leachate spreading in homogeneous (modified after Christensen et al. (2000)) and heterogeneous geologic settings (modified after Kessler et al. (2012)) show different potentials for contamination discharge into stream.

Typically, the development of a landfill leachate plume is complex even when considering homogeneous sandy aquifers (e.g. Bjerg et al., 1995; Lyngkilde and Christensen, 1992b). Hence, classic concepts can not be applied on complex hydrogeochemical settings such as clay till, where vertical fractures and horizontal sand lenses and stringers pose preferential flow paths with anaerobic conditions (Figure 1).

Leachate spreading in clay till is limited to the preferential groundwater flow paths and eventual places of discharge into streams. Streams can be groundwater-gaining, groundwater-recharging if they lose water to groundwater, or intermediate (Winter et al., 1998). One of the two latter options allows the discharge into the stream from sand lenses with close contact to the stream. If this is the case, concentration of the discharged leachate in confined pathways of clay till is expected to be higher than e.g. in a landfill leachate plume in sandy deposits, since dispersion of contaminants is restricted within the pathways. Limited spatial distribution of landfill leachate in such constrained conditions pronounces the importance of a good strategy for proper construction and location of monitoring wells in the field.

Since landfills typically evolve over longer periods, there are usually enough data on terrain, geology, waste disposal development, waste composition and groundwater chemistry at institutions involved in the waste disposal management to formulate the overall conceptual model. A desktop study based on these data and eventual interviews with local community can be undertaken to obtain a general understanding of hydrogeology and water chemistry prior to the field measurements, formulating the overall concept of the landfill (Thomsen et al., **I**).

2.1.1 Geology, hydrogeology and groundwater chemistry

Contaminants can be diluted in groundwater or bound to soil. A common way to take geological and groundwater samples along the depth profile is to drill a well (~60 mm in diameter) with a 0.5-1 m screen in the bottom. Although this technique is resource-consuming, it provides direct geological samples along the drilling profile, and poses a robust and reliable field installation for long-term monitoring (Thomsen et al., **I**). Drawback of the drilled wells method is that it works only if the terrain is easily accessible for the heavy drilling equipment, which is not the usual case in wetlands (Figure 2).

Wells of 30-40 mm in diameter can be directly pushed – driven into the ground, with shorter installation time and less environmental disturbance than the drilled wells (Geoprobe®). A relatively smaller pneumatic field equipment than the one for drilling has a possibility to penetrate hard waste layers and to access steep landfill slopes or places of dense vegetation (Thomsen et al., **I**; Milosevic et al., **II**) but it has the same limitation of accessing wetlands.

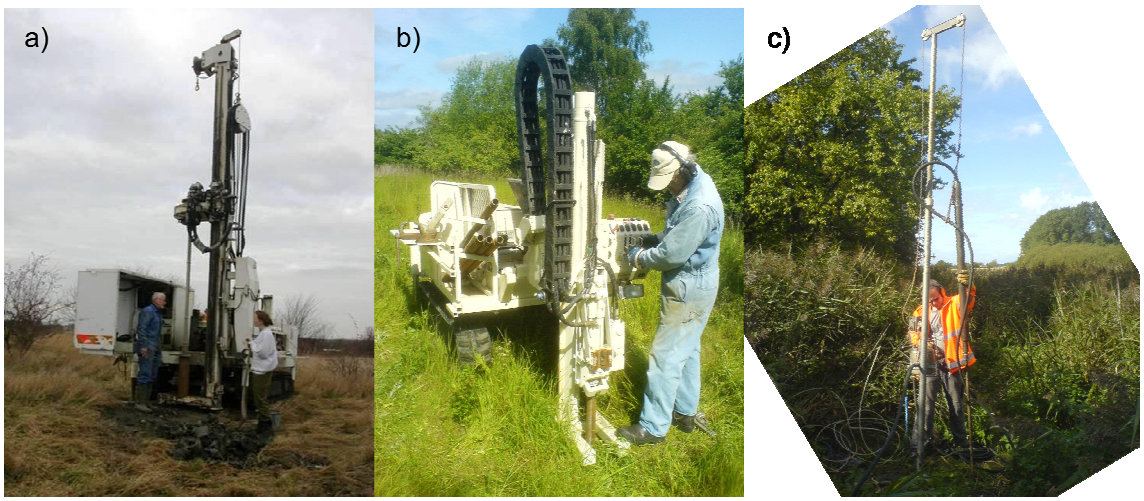

Figure 2: Equipment for a) drilling, b) driving (Geoprobe®) and c) manual driving of wells for groundwater sampling

Smaller wells of 2.5 mm in diameter can be quickly driven by pneumatic hand equipment (Kjeldsen et al., 1998) even on hardly accessible places such as wetlands. They also provide a possibility of rough characterization of geologic profiles based on the water presence and resistance of soil to the driving. Sand lenses of clay till are poorly researched but a resolution of 25 cm should suffice for 50-100 cm thick lenses (Gerber et al., 2001; Hendry et al., 2004; Nilsson et al., 2001) and a resolution of 50 cm for should suffice for sand and peat deposits. Vertical variation of chemical parameters within the preferential pathways can increase with the pathway thickness, although the values are not expected to be higher than one order of magnitude i.e. the variation within the preferential pathways should not impact the contaminant mass discharge considerably. High horizontal distribution of the sampling points and frequent re-sampling in different seasons would decrease the uncertainty of vertical data variation. Groundwater in confined settings of clay till can be identified and subsequently sampled at different depths, whereby hydraulic potentials can be measured specifically for the sand lenses, and groundwater flow fields can be estimated (Milosevic et al., **II**). Smaller driven wells can be additionally installed in a dense

sampling network (Figure 3) in order to provide maps of e.g. preferential groundwater or contaminant flow.

Drilled wells are suitable for characterization of the 20-40 m deep aquifer (Thomsen et al., **I**; Milosevic et al., **II**). Larger driven wells can be applied when penetrating the thick waste layers is needed for characterization of landfill leachate hotspots. Smaller driven wells are suitable for characterization of the shallow aquifer, delineation of the landfill leachate and subsequent groundwater sampling campaigns (Milosevic et al., **III**).

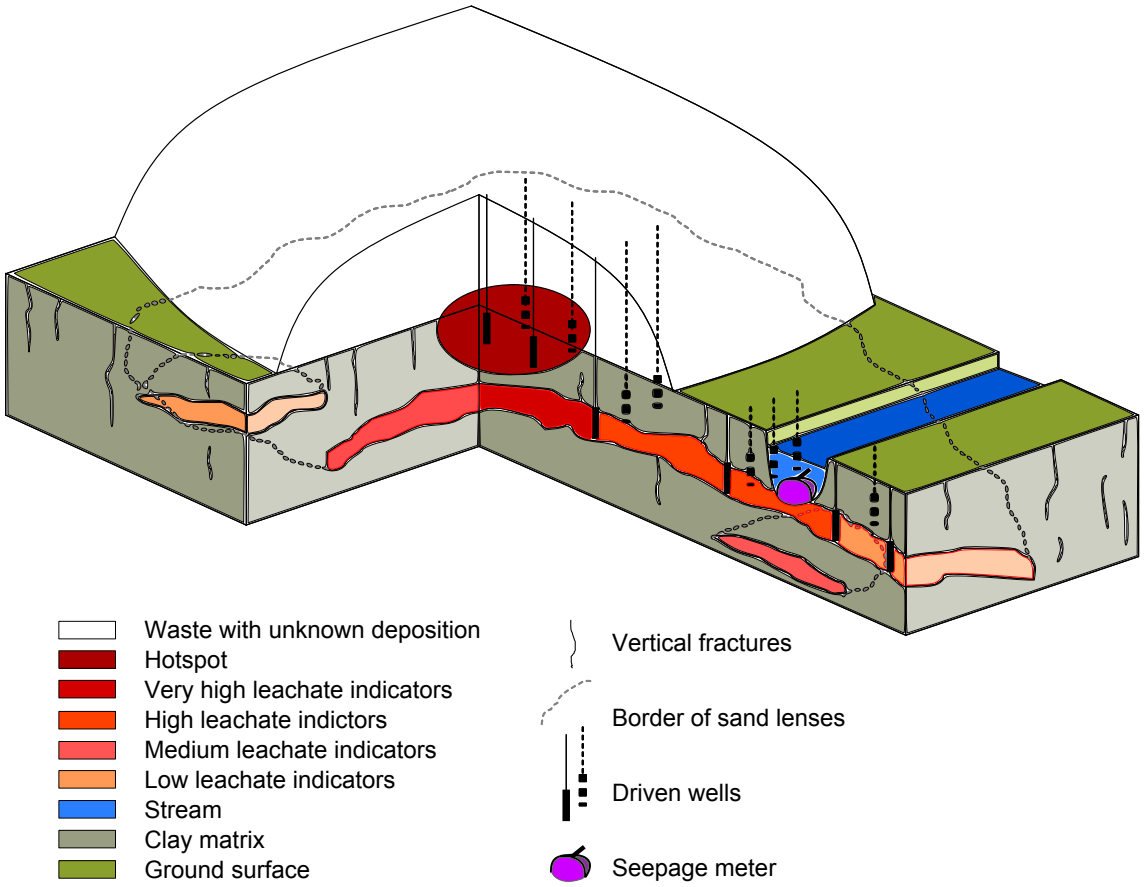

Figure 3: Conceptual hydrogeologic model of a landfill site in clay till. A sand lens is in a close contact with a stream, posing the preferential pathway for landfill leachate. Transects of driven wells are placed perpendicular to the groundwater flow from the hotspot of pollution towards the stream, ending with a point unaffected by landfill leachate on the other side of the stream. Seepage meter is placed in the streambed for sampling of the discharged groundwater.

Leachate indicators, redox parameters and xenobiotic compounds can be analyzed as initial parameters of the concept using the drilled or driven wells. The field work includes i) the delineation of groundwater plume between the

landfill and impacted water bodies and ii) the identification of the preferential pathways of contamination between the delineation transect and the exact hotspots of pollution (Milosevic et al., **II**). The final sampling installations in the field should be located in all parts of the landfill site (hot spot, groundwater transport routes, transition zone to the surface water and not-impacted locations for background values) in the way that contaminants can be analyzed both along and across the contamination flow (Figure 3). Correct placement of the wells is actually an iterative process where knowledge on local geology, leachate composition, redox conditions and contaminant transport routes continuously improve.

2.1.2 Chemistry of discharged groundwater and stream hydrology

Discharged groundwater can be sampled for chemical analysis in the groundwater-surface water transition zone by i) hand-pushed piezometers, ii) multilevel samplers (Rivett et al., 2008a) and iii) seepage meters – half-drums placed in the streambed (Brodie et al., 2009). The discharged groundwater in clay till can be sampled below the streambed, within the sand lenses, by hand-pushed steel piezometers (Milosevic et al., **II**). Piezometers also allow measurement of hydraulic head, which is not the case with other two methods. Additionally, the groundwater sampling by multilevel samplers and seepage meters can be challenging in very clayey or muddy streambed. Nevertheless, the zones of high hydraulic potential for groundwater discharge can be located by a smaller version of the chamber or by temperature gradients of the streambed, which optimizes the usage of the samplers (Thomsen et al., **I**).

Hydrologic and chemical conditions in temperate/cold climate conditions are expected to vary more in the stream than in groundwater and sampling campaigns should cover all seasons of the year. Automatic stream level station can be used for monitoring the hydrologic conditions over larger time periods (Milosevic et al., **II**). Thereby the levels can be expressed as stream discharge – the key parameter in estimation of leachate dilution in the stream i.e. chemical impact of landfill leachate on the stream. Simple grab sampling in the mid stream suffices for the chemical analysis of stream water (Martin et al., 1992), whereas the stretches upstream and downstream of the immediate landfill impact provide an estimate of the background and level-off concentrations, respectively.

2.1.3 Quantification of contaminant mass budget and discharge

Documenting of contaminant mass loss in the field is needed to constitute the initial conceptual site model (Table 1). The most concentrated inorganic and xenobiotic compounds detected throughout the site are expected to have the highest impact on the chemical status of the surface water and should be included in this step of attenuation assessment. Guidance in choosing the appropriate method for documenting of contaminant mass loss issued by National Research Council (2000) and reviewed by Illman and Alvarez (2009) is based on the needed level of data analysis i.e. on the level of hydrogeologic complexity, contaminant concentrations and contaminant degradability. Mass budgeting and mass discharge quantification are referred as the most appropriate methods in case of small-scale heterogeneity in clay till and medium-high concentrations of contaminants which degrade under most or limited conditions. The conceptual model of hydrogeology and water chemistry could be potentially upgraded to numerical or analytical models. However, it was beyond the scope of the thesis.

The choice of quantification methods for contaminant mass discharge (mass/time) depends on the site conditions and purpose of the research (Troldborg et al., 2010) and the usual way is by multiplying water flow rate, contaminant concentration and discharge area perpendicular to the flow. Estimating mass discharge of recalcitrant chemicals from heterogeneous contaminated sites to the groundwater is affected by large uncertainty and doable only on an individual basis for every site (Schwarzenbach et al., 2010). Mass discharge of landfill leachate contaminants into groundwater was studied for chloride and phenoxy acid pesticides by Tuxen et al. (2003) and for chlorinated solvents by Ptak et al. (1998). Contaminant mass discharge can be a basis of a box model of mass balance that comprises the whole landfill site (Figure 4). Mass discharge can be calculated by for each side of the box by using concentration and water discharge estimates (Thomsen et al. **I**). Furthermore, contaminant mass discharge can be measured for the groundwater discharge zone in the clay till area, where contaminants enter the stream. Finally, mass discharge can be estimated more detailed for the small scale heterogeneities in clay till geology and recalcitrant xenobiotic compounds (Milosevic et al., **II**).

Mass discharge and chemical impact of landfill leachate-impacted groundwater flowing into surface water was studied for chloride, nitrate and ammonium by Douglass and Borden (1992) and for sulphate by Scholl et al. (2006). The mass

discharge zones of xenobiotic compounds are established as a direct link between the landfill and a stream by Milosevic et al. (**II**).

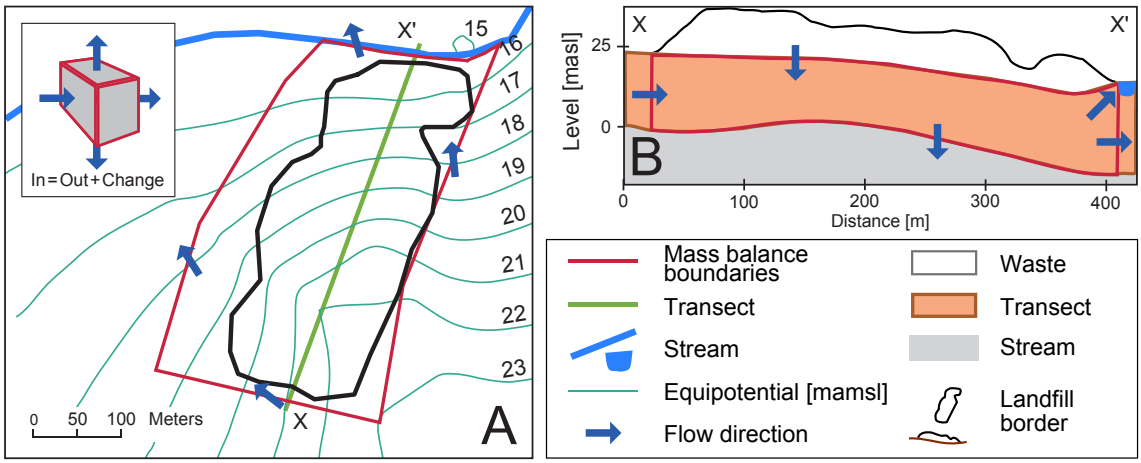

Figure 4: Mass balance model of a landfill based on mass discharge estimates through a control box placed under the landfill. The top of the box was formed by the hydraulic potential surface in the upper saturated zone, while the interface between the limestone aquifer and the upper saturated zone formed the bottom. The sides of the box were represented by the four borders of the landfill and mass discharge into the stream was additionally measured (modified from Thomsen et al. (**I**)).

For quantification of groundwater discharge into the surface water, multiple, alternative and complementary field methods such as Darcy's flow calculations, seepage meters or tracers (chemical, isotope or temperature) are recommended by different authors in order to overcome uncertainties associated with any of the chosen techniques (Andersen and Acworth, 2009; Baxter et al., 2003; Halford and Mayer, 2000; Hatch et al., 2006; Kalbus et al., 2006).

Darcy's flow comprises the calculation of one-dimension groundwater flow at a single point (Eq. 1). The total discharge, Q [m³/s] is equal to the product of the hydraulic conductivity, K [m/s], the cross-sectional area to flow, A [m²], and the hydraulic gradient i. It can detect small potentials for groundwater discharge independently on the depth below the streambed but it heavily depends on the assumed values for water conductivity of different soil types and on the interpolations from point of measurement to the discharge area, which can be uncertain in clay till.

$$Q = K \cdot A \cdot i \qquad (1)$$

The seepage meter is another method for point-measurement of groundwater discharge. In contrary to Darcy's flow, where the maximal potentials can be obtained, seepage meters collect the actual groundwater discharge and these values can be deemed minimal. In addition to the uncertainty of interpolation from point to the area, the seepage meters have several possible drawbacks in practical use (Brodie et al., 2009) and clogging by fine sediments is seen as the most important one in wetlands and slow streams.

Temperature gradients in the streambed can be used as a tracer for delineation of groundwater discharge zones and quantification of the discharge into stream (Anderson, 2005). The gradient is higher and uncertainty of the method is lower in summer and winter, when stream temperature is substantially different from the generally constant groundwater temperature. Point measurement of temperatures is less uncertain than Darcy's flow and seepage meters since the thermometer equipment is not fixed in the streambed but used only as an inspection tool, providing larger amount of data. The temperature gradient in different soil types in clay till settings (clay, sand and peat) is related to groundwater flow by Milosevic et al. (**II**) by means of an analytical solution of (Schmidt et al., 2007). Temperatures gradients can be related to larger areas and longer periods of time (Kalbus et al., 2006), but such approach demands a more extensive data analysis.

Conservative tracers can be used for quantification of groundwater discharge but the groundwater flow paths should be precisely known for such calculation (Kalbus et al., 2006). Thus the usage of tracers is not suitable for iterative investigation of unknown flow paths in complex settings. However, Milosevic et al. (**III**) used water isotopes as a qualitative tool in an established groundwater sampling network, estimating the origin of ground- and stream water samples and revealing preferential flow paths within a groundwater discharge area.

Challenges of groundwater discharge measurement in the scale of sand lenses of clay till can be overcome by a simultaneous use of point measurements of Darcy's flow, seepage meters, streambed temperature gradients (Kalbus et al., 2006; Milosevic et al., **II**) and water isotopes (Milosevic et al., **III**). The biggest uncertainty in application of point measurements of groundwater discharge lies in extrapolation of data to discharge areas. However, sand lenses of clay till form discharge areas that are abruptly outlined by impermeable peat or clay, which minimizes the uncertainty of the extrapolation.

Contaminant mass discharge, calculated from groundwater discharge, contaminant concentration and the discharge area, is the key parameter in estimation of chemical impact from old landfills on ground- and surface waters (Basu et al., 2006). Chemical impact from clay till area on the stream can be calculated as a ratio between groundwater mass discharge and the intrinsic mass discharge in the stream, considered as the background (Milosevic et al., **II**).

2.2 Improvement of the conceptual site model

2.2.1 Geochemical and chemical indicators

The conceptual landfill site model of hydrogeology and water chemistry can be improved through *in situ* measurement of specific geochemical or chemical footprints – indicators of natural attenuation. Several potential methods indicate degradation processes in the groundwater and the interdependency of the processes with contaminant transport and reactivity (Table 2).

Table 2: Geochemical and chemical *in situ* indicators of natural attenuation in landfills (Bjerg et al., 2011; Bombach et al., 2010; Cozzarelli et al., 2011; Elsner, 2010; Illlman and Alvarez, 2009; Reitzel, 2005).

	Geochemical indicators of natural attenuation at landfill sites
1	Depletion of electron acceptors (oxygen, nitrate, manganese and sulphate), formation of ferrous iron and methane, sulphide, production of hydrogen
2	Increase of dissolved inorganic carbon and alkalinity
3	Increase of BOD_5/COD ratio (biological oxygen demand during 5 days / chemical oxygen demand) in recent landfills (acidic phase) and a decrease in old landfills (methanogenic phase)
	Chemical indicators of natural attenuation at landfill sites
1	Demonstration of contaminant decrease over distance
2	Demonstration of contaminant concentration decrease over time
3	Detection of metabolites or by-products
4	Changes in metabolite and enantiomer ratios and isotope values
5	Changes in enantiomer or isotope fractionation

The difference in natural attenuation of xenobiotic organic compounds between landfill leachate with mixtures of contaminants and contaminated sites with e.g. homogeneous BTEX contamination is that dissolved organic carbon (DOC), and not the contaminants, is the driver for the formation of redox zones in landfill leachate plumes (Christensen et al., 2001). DOC comprises a vast majority of carbon content in the landfill leachate and is the main electron donor in redox zonation, with bicarbonate as by-product of the reaction (e.g. Baun et al., 2004). Thus, redox zonation can not be coupled with transformation of xenobiotic

organic compounds at landfill sites. Geochemical analysis of redox parameters is compulsory for characterization of landfill sites, but additional analyses for estimation of xenobiotic organic compounds' degradation are also required.

Chemical indicators of natural attenuation are related to the contaminants (Table 2), often providing a quantitative estimation of their degradation. Leachate plumes at old landfills are in a relatively steady state, contrary to e.g. a recent accidental pollution (Kjeldsen et al., 2002). The steady state of the plume prevents usage of the tracking of contaminant propagation as chemical indicator of natural attenuation but a concentration decrease over distance is a usual approach. Decrease of contamination in the stable methanogenic leachate where e.g. electron acceptors are depleted and alkalinity is high (Christensen et al., 2001) can be observed only on a large time scale (Bjerg et al., 2011).

Ratios of chemical compounds from certain metabolic pathways can be used for fate assessment of these compounds (Reitzel et al., 2004). Products of the sequential dechlorination of chlorinated solvents (Figure 5) or potential transformation products of phenoxy acids (Figure 6) can be used for calculations of the ratios. Impurity content of compounds from industrial production has to be regarded as the worst-case ratio (Reitzel, 2005). Higher values for the ratio indicate attenuation of the compound while the impurity is recalcitrant, its higher attenuation compared to attenuation of the impurity or its transformation to the impurity.

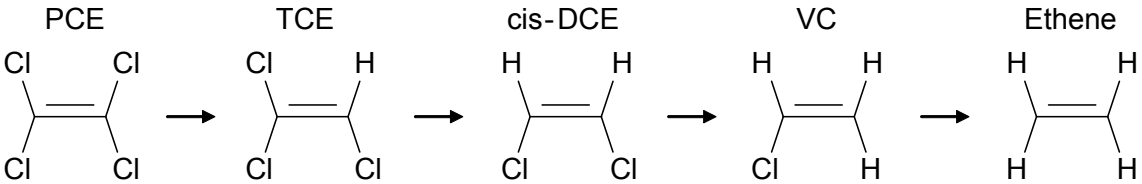

Figure 5: Structural formulas of chlorinated solvents: tetrachloroethene (PCE), trichloroethene (TCE), *cis*-1,2-dichloroethene (cis-DCE) and vinyl chloride (VC) and ethene in sequential dechlorination reaction

Ratios of enantiomers – isomeric molecules that differ only in the spatial orientation of their atoms can be used as another *in situ* degradation indicator when the contaminant has a stereoisomeric structure. Enantiomers occur in most of the investigated phenoxy acids (Figure 6). Enantiomers are compound-specific and often specific for certain environmental conditions (Harrison et al., 2003), whereas metabolites can derive from different parent compounds. Enantioselective transformation of phenoxy acids depending on redox conditions

was shown in laboratory conditions also by Reitzel (2005) and in the field by Harrison et al. (1998) and Williams et al. (2003). However, the opposite was shown in a field injection study by Rügge et al. (2002).

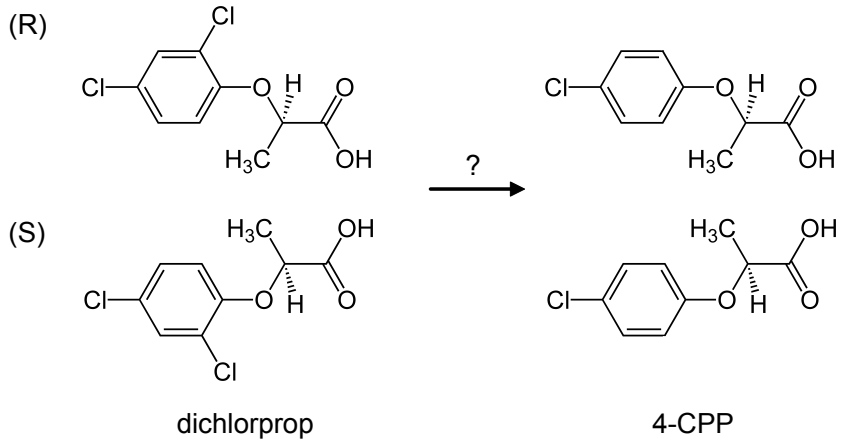

Figure 6: Structural formulas of right (R) and left (S) enantiomer forms of phenoxy acids: pesticide dichlorprop and its potential degradation (dechlorination) product 4-CPP

Enantiomer concentration ratios (ER) can not be calculated when left (S) enantiomer form is depleted (Eq. 2). Nevertheless, enantiomer excess (EE) can be calculated within the range of -100 – 100 % (Eq. 3).

$$ER = \frac{[R]}{[S]} \tag{2}$$

$$EE = \frac{[R]-[S]}{[R]+[S]} \tag{3}$$

Chemical structures of mixed organic compounds in the landfill leachate are variable and it is not always possible to perform analyses e.g. of enantiomer concentration. Compound-specific isotope analysis (CSIA) is a tool with an increasing number of quantitative *in situ* applications, suitable for application to a range of compounds at once (Elsner, 2010). It detects ratios between heavier and lighter molecules in the remaining substrate in biochemical reactions, which is the result of the phenomenon of preferential cleavage of bonds with lighter isotopes. The ratio between heavier and lighter molecules changes over time and, similarly to enantiomers, the fractionation process is compound-specific and may change with redox conditions. The disadvantage of CSIA to enantiomer analysis is that it has a higher analytical uncertainty.

CSIA is not applicable in cases of a non-significant isotope fractionation during the microbial degradation or a lack of analytical procedures for specific

investigated compounds. A lack of supportive laboratory studies on microbial fractionation of emerging and poorly studied compounds can hamper the quantification of the attenuation. Only a few fate studies using CSIA considered hydrogeologic heterogeneous systems such as fractured rock (Chartrand et al., 2005; Spence et al., 2005), clay-rich soils (Blessing et al., 2009) or clay till (Damgaard, 2012; Hunkeler et al., 1999; Milosevic et al., **II**).

2.2.2 Choice of methods for fate assessment

The choice of methods for *in situ* fate assessment depends mostly on the type of the investigated compounds (Table 3). Fate assessment of key xenobiotic compound groups in the landfill leachate – phenoxy acid pesticides, chlorinated solvents and petroleum derivatives (benzene, toluene, ethylbenzene, otrho-, meta- and para-xylene (BTEX)) was reviewed by several authors (Bjerg et al., 2011; Bombach et al., 2010; Christensen et al., 2000; Christensen et al., 1994; Everett et al., 2002; Kjeldsen et al., 2002; Mattes et al., 2010; Newell and Aziz, 2004; Rivett and Thornton, 2008b; Scow and Hicks, 2005).

The fate assessment methods for these three groups of xenobiotic compounds at old landfill sites with anaerobic conditions are reviewed in Table 3. General geochemical characterization has been usually underpinned by microbiological and molecular analyses as the second fate assessment method. Long-term decrease of contaminant concentrations at old landfills is observable in the scale of decades or even centuries (Bjerg et al., 2011) and it is estimated only if previous studies or a monitoring at the site exist. Metabolite concentrations have been frequently analyzed for all selected contaminant groups and enantiomer analysis has frequented for phenoxy acids.

Only few studies using CSIA dealt with landfill leachate. Namely Richnow et al. (2003) investigated BTEX and Milosevic et al. (**III**) investigated all selected contaminant groups. CSIA studies on BTEX and chlorinated solvents at other sites than landfills, which can be used to support the findings from landfill leachate, are numerous. For instance BTEX was studied by CSIA at a former gas factory (Morasch et al., 2011), chlorinated solvents at a former military base (Morrill et al., 2005) or both BTEX and chlorinated solvents at a former industrial site (Nijenhuis et al., 2007). Milosevic et al. (**III**) dealt with CSIA, metabolite and enantiomer analysis in a complementary way, assessing the compound-specific *in situ* degradation of selected contaminants without supportive microbial studies.

Table 3: Methods for fate assessment of phenoxy acids, chlorinated solvents and BTEX applied in selected studies on old landfill leachate with anaerobic conditions

Selected references listed in a chronological order	Contaminant groups			Methods for fate assessment of selected contaminant groups						
	Phenoxy acids	Chlorinated solvents	BTEX	Concentration decrease over distance	Long-term concentration decrease	Metabolite analysis	Enantiomer analysis	Contaminant CSIA	Micro- and molecular
Lyngkilde and Christensen, 1992a	x		x	x		x			
Lesage et al., 1993		x	x			x			x x
Nielsen et al., 1995		x	x						x x
Rügge et al., 1995			x	x		x			
Harrison et al., 1998	x								x
Zipper et al., 1998	x			x			x		
Bjerg et al., 1999		x	x						x x
Rügge et al., 1999a	x			x					x
Rügge et al., 1999b		x	x	x		x			
Bright et al., 2000		x	x			x			x
Eganhouse et al., 2001		x	x	x		x x			
Richmond et al., 2001		x	x	x					x x
Röling et al., 2001			x						x
Skubal et al., 2001		x	x		x x	x			x x
Tuxen et al., 2003	x			x					x
Baun et al., 2003	x		x	x x	x x	x x			
Harrison et al., 2003	x						x		x
Richnow et al., 2003			x	x				x	
Tuxen et al., 2003	x			x		x			x
Williams et al., 2003	x			x			x		x
Gonsoulin et al., 2004		x		x	x	x			
Reitzel et al., 2004	x			x	x	x			x
Ledin et al., 2005			x			x			
Reitzel, 2005	x			x		x	x		x
Tuxen et al., 2006	x					x			x
Botton et al., 2007			x	x					x
Cozzarelli et al., 2011		x	x	x x	x x	x x			
Staats et al., 2011			x			x			x
Milosevic et al., **III**	x	x	x	x		x x	x	x x x	

2.3 Finishing of the conceptual site model

Microbial studies on samples directly taken in sediment or waste are considered to be the last supportive proof of natural attenuation (Table 1). Microbial studies are based on cultivation techniques, *in situ* microcosms or functional genes (Bombach et al., 2010). Even though the environmental conditions from the field are being disturbed during the sampling and the further analytic procedures can bias the results, the microbial data show evidence of biodegradation (Illman and Alvarez, 2009). The most reliable approach for finishing the conceptual model is to add microbial indicators of natural attenuation to other fate assessment methods in a dialectic, complementary manner. An additional potential input of microbial methods for the model is to provide more insight into the biochemical mechanisms of degradation, into the eventual changes of microbial degradation according to alterations of environmental conditions e.g. destruction of microhabitats in sampling, into the complex interactions between degrader species and into the solutions to challenge of duplicating environmental conditions in the laboratory (Illman and Alvarez, 2009; Weiss and Cozzarelli, 2008). However, such insight is beyond the purpose of a standard conceptual site model and will not be addressed.

Microcosm studies can be either on a level of microbial community or on a level of selected microbial strains (Table 4). Although the selected strains can be key players in the attenuation process and the methods exist for quantification of the attenuation, the disadvantage when analyzing the selected strains is that the selection process can oversimplify the conceptual model. Further, the modeling can not always be performed due to many obstacles e.g. >99 % of the strains found in nature are not cultivable (Kaeberlein et al., 2002). On the other hand, community level analyses provide easier quantification and estimation of interactions between the community groups/members. However, such analyses can be insufficient for the degradation of specific recalcitrant compounds where few specialized strains can play the only role (Weiss and Cozzarelli, 2008).

Microbial communities can be analyzed for changes in the catabolic genes concentrations (DGGE, T-RFLP, DNA-microarrays), for microbial metabolic adaptation or selective degradation relative to more stable chemicals (Illman and Alvarez, 2009). Both communities and strains can be analyzed on the cell level or on the molecular level, depending on the purpose (Table 4).

Table 4: Microbial and molecular analyses of microcosm samples for provision of direct proofs of natural attenuation, modified after Illlman and Alvarez (2009)

Microbial analysis	
	Degradation of contaminant of concern
	Enantiomer or isotope fractionation rate
	Estimation of metabolic activity
	Growth assessment e.g. by flow cytometry
Molecular analysis	
Target	
16S rRNA	Computing phylogenetic relationships and identification of novel organisms
	Visualization, counting and biomass estimation of specific strains by fluorescent *in situ* hybridization (FISH)
DNA	Identification of communities, community members and catabolic genes by quantitative polymerase chain reaction (qPCR)
mRNA	Identification of the expressed genes by qPCR
Enzymes	Substrate degradation by enzyme extracts
Phospholipids	Estimation of living biomass of different communities
	Evaluation of microbial stress and nutritional status

The biggest disadvantage in microcosm studies in heterogeneous settings is a practical issue of representative sampling in often inaccessible field conditions, particularly in the anaerobic compartment of the landfill. Extrapolation of microcosm results from few sediment samples to the field site scale might be therefore uncertain. However, this can be superseded by a parallel use of indirect methods and as for any upscaling, modelling is inevitable (National Research Council, 2000). Sampling locations in aerobic conditions such as in the streambed are easier to identify, usually easier to approach and potentially high degradation activity in the groundwater-surface water transition zone can be estimated. Sediments from the transition zone were studied by Batioglu-Pazarbasi et al. (**IV**) with an ambition to prove this interface as the place of specific gene diversity and enhanced degradation activity. The aerobic microcosm mineralization study was performed for selected phenoxy acids on samples taken in groundwater discharge zone of clay till on both community and specific strain level, investigating mineralization, cell abundance and genetic diversity of specific degraders. A follow-up study representing the conditions in the larger, anaerobic part of the investigated landfill site or the conditions of steep chemical gradient in the hyporheic zone was not done.

3. Fate of key organic contaminants

3.1 The study site

3.1.1 Landfill history

The objectives of this study were set with the ambition of obtaining a more thorough knowledge of attenuation processes of landfill leachate at clay till settings and in the transition zone between ground- and surface waters. The field activities were performed at the Risby Landfill, which is an example of an old landfill formed without control of waste disposal on clay till terrain, with a groundwater-gaining stream in its close vicinity (Figure 7).

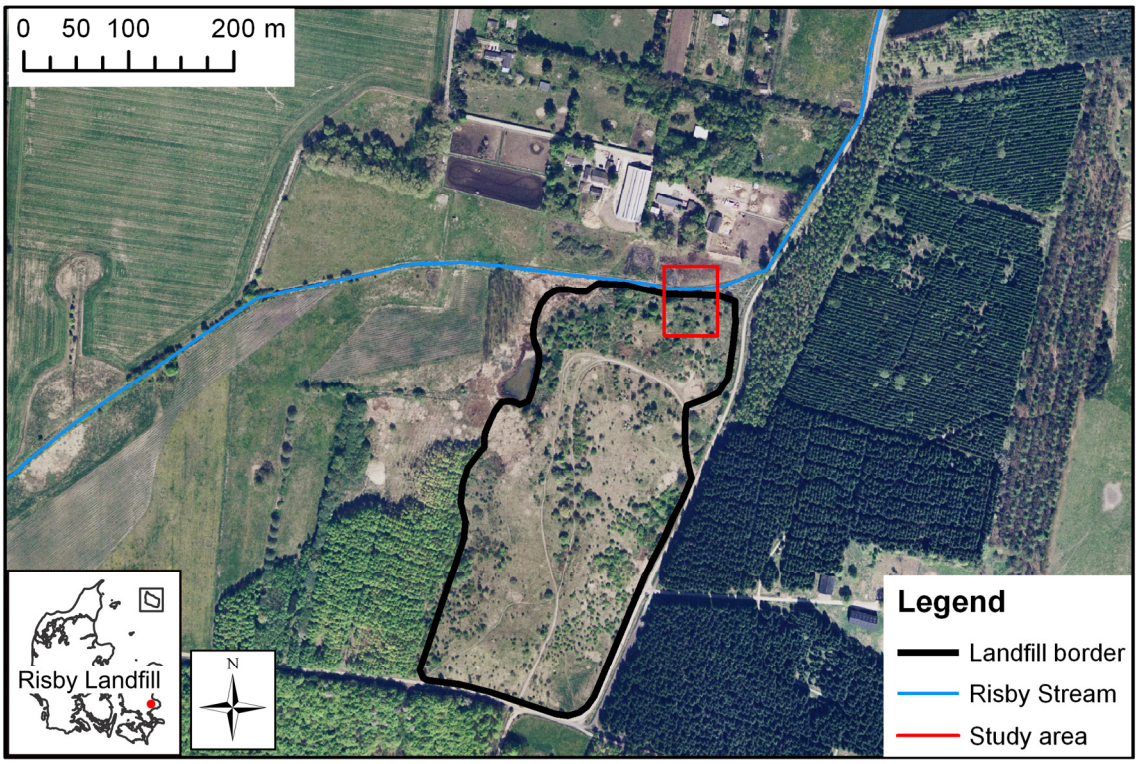

Figure 7: Risby Landfill, close to Copenhagen, Denmark. The old landfill (black line) without liners for the leachate is situated in the close vicinity of a local Risby Stream (blue line). Study area encompassing relevant hotspots of pollution, geologic settings and end-recipient of landfill leachate contaminants, the stream, is indicated as the red line (modified after Milosevic et al. (**II**)).

The waste was initially deposited in the area of a former wetland, close to today's Risby Stream, probably causing discharge of xenobiotic compounds from landfill leachate into the stream. Long-term pollutants phenoxy acid pesticides, BTEX and chlorinated solvents (Figures 5, 6 and 10), were detected in groundwater monitoring prior to this study. Natural attenuation of these contaminant groups

was quantified by Milosevic et al. (**III**) using a conceptual model. The model included geochemical and water chemistry data, identified groundwater discharge zones and quantified mass discharge for phenoxy acids (Thomsen et al., **I**; Milosevic et al., **II**).

3.1.2 Redox conditions and groundwater pathways

Redox processes in the landfill leachate are driven by oxidation of DOC (Christensen et al., 2001). During this process electron acceptors are depleted and redox conditions gradually change from methanogenic and sulphate-reducing in the hotspot to nitrate-reducing and aerobic in the outskirts of the plume (e.g. Bjerg et al., 2011). Redox conditions in the confined groundwater pathways of clay till at the Risby Landfill are anaerobic, methanogenic in the hotspot and slightly less reduced close to the stream (Milosevic et al., **II**).

Identification of groundwater pathways is necessary for fate assessment of contaminants along the pathways. Mobile contaminants can be tracked and potential degradation processes along the groundwater flow direction can be identified based on the dilution factor of conservative tracers, e.g. chloride (Lyngkilde and Christensen, 1992a). Groundwater pathways in clay till were identified for such calculations using chloride and water isotopes (Milosevic et al., **III**). Western and eastern groundwater pathways that connect the hotspot with the groundwater-surface water transition zone were distinguished (Figure 8) and mixing process of groundwater from two pathways was identified in the hyporheic zone. The exact separation line between the groundwater pathways could not be distinguished and two separation lines formed a strip with the intermediate values of conservative tracers.

3.2 Fate of phenoxy acids

Phenoxy acid pesticides and their transformation products can be analyzed by several methods due to their specific structure (Figure 6). They are chiral molecules and have low sorption coefficients (Hansch et al., 1995). This allows the use of different analytic methods (metabolite, enantiomer and isotope analysis) to assess their environmental fate, but also to track their degradation along the groundwater pathways. However, not all pesticides are chiral and not all processes of pesticide transformation are enantiomer-specific.

Phenoxy acids are recalcitrant in strongly reduced conditions such as in the landfill leachate (Broholm et al., 2001; Buss et al., 2006; Harrison et al., 1998; Reitzel et al., 2004). However, their (R)-enantiomer-preferential degradation can be expected at nitrate-reducing conditions and very quick (S)-enantiomer-preferential degradation can be expected at aerobic conditions such as in the streambed (Harrison et al., 2003; Williams et al., 2003). Preference to one of the enantiomer forms depends on the presence of oxygen (Reitzel, 2005; Rügge et al., 2002). However, the enantiomer and isotope enrichment factors are still poorly quantified. The carbon-based CSIA has recently been applied for microbial degradation assessment of different pesticides (Badea et al., 2009; Penning et al., 2010; Reinnicke et al., 2012) and the method was very recently optimized for phenoxy acids (Reinnicke et al., 2010). Milosevic et al. (**III**) applied CSIA for the fate of phenoxy acids *in situ*, but the enrichment factors stayed undetermined.

3.2.1 Fate of phenoxy acids in anaerobic conditions

Despite the presence of different phenoxy acids throughout the investigated part of the landfill site only 4-CPP (CAS RN 3307-39-9) and dichlorprop (CAS RN 120-36-5) appeared in constant concentrations and consistently on the analyzed locations (Figure 8). 4-CPP was the only phenoxy acid found ubiquitously throughout the site and in high concentrations, also outside the hotspot (Figure 8a). It is an impurity in industrial production of dichlorprop with 5 % estimated content (worst case) (Reitzel, 2005). 4-CPP is also a potential metabolite product of dichlorprop (through dechlorination), but that metabolic pathway has not yet been proven (Reitzel et al., 2004; Tuxen et al., 2003). Ratio between 4-CPP and dichlorprop in the place of the highest concentrations was 0.2, which is 4 times higher than the worst-case. This ratio was exceeded even more in other groundwater samples, indicating a reductive dechlorination of dichlorprop.

Enantiomer excess (EE) shows the ratio of two enantiomer forms. For instance, zero value is measured when the forms are in equal concentrations (racemic mixture). Measured $EE_{dichlorprop}$ of 0±1 % in the hotspot wells suggested no/low microbial enantioselective degradation of dichlorprop (Figure 8b). It is contrary to indications of metabolite ratio that dichlorprop was degraded to 4-CPP in anaerobic conditions. On the other hand $EE_{4\text{-}CPP}$ in the hotspot wells was higher than zero (49%), supporting the finding of metabolite ratio. $EE_{4\text{-}CPP}$ stayed high downgradient of the hotspot, indicating steady (S)-preferential, anaerobic degradation of 4-CPP along the flow path. However, the $EE_{4\text{-}CPP}$ lower than 0 in

shallow groundwater samples close to the stream revealed occasional (R)-preferential, possibly aerobic degradation of 4-CPP. $EE_{4\text{-CPP}}$ changed along the groundwater flow path according to alternated redox conditions. The alterations of degradation pathways were revealed on places where metabolite ratio could not be calculated (dichlorprop depleted) and where redox conditions did not show substantial changes in several field campaigns. Enantiomer analysis was advantageous in shallow groundwater wells where analysis of metabolites and redox parameters did not indicate any change of degradation mechanism.

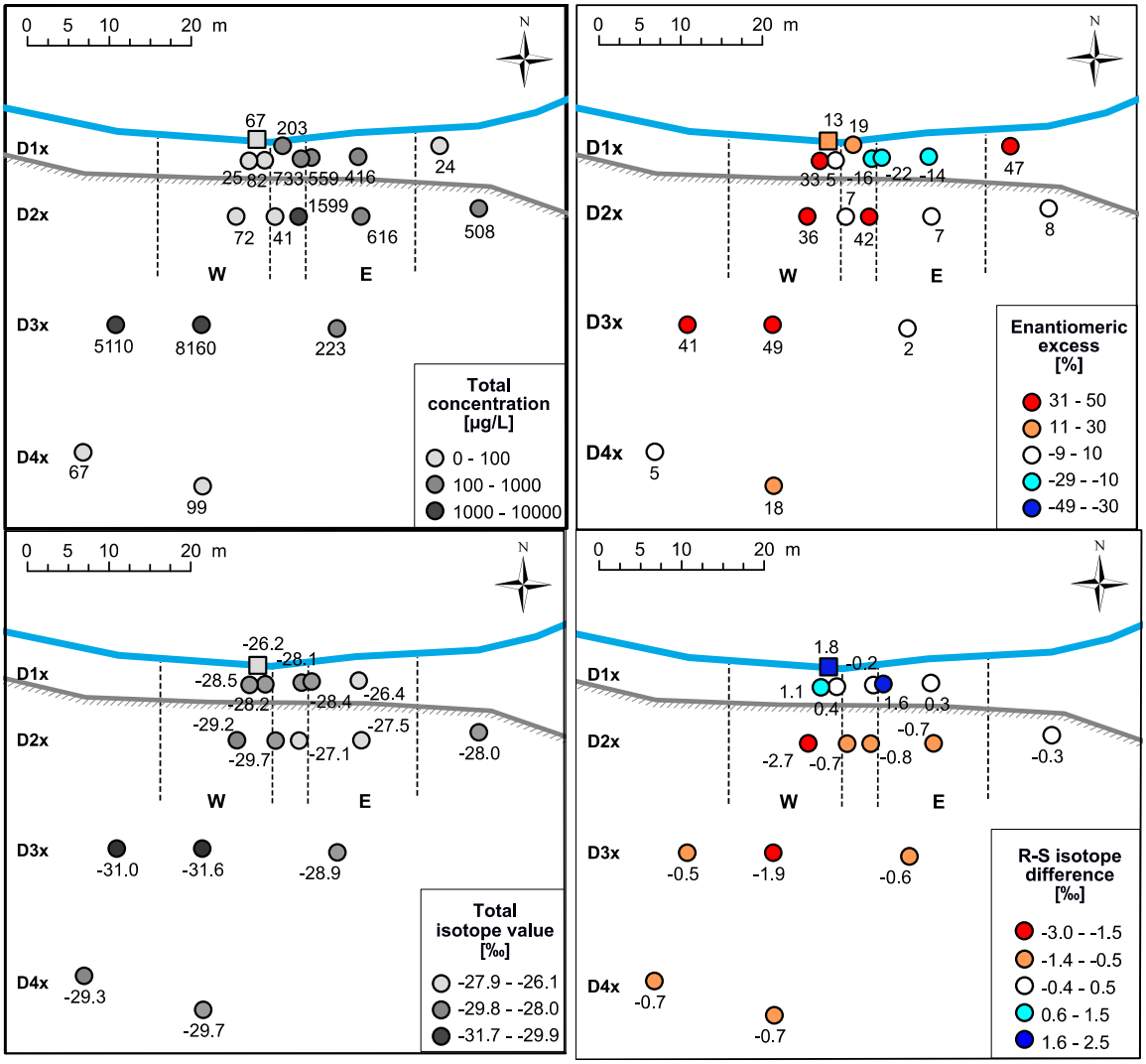

Figure 8: Maps of 4-CPP at D1x-D5x sampling transects in the study area of the Risby site. Western and eastern groundwater pathways are marked W and E and seepage meter is shown as the square in the stream in the end of the W pathway (Milosevic et al., **III**).

a) Total concentration [µg/L] (sum of right (R) and left (S) enantiomer concentrations)

b) Enantiomeric excess of (R) (red) and (S) (blue) enantiomer

c) Total isotope values [‰] (of the total (R) and (S) enantiomer concentrations)

d) Difference of isotope values between (R) and (S) enantiomers

Dichlorprop and 4-CPP are assumed to have a common origin. The isotope value ($\delta^{13}C$) shows the ratio of the preferentially degraded light (containing only ^{12}C) contaminant molecules to the heavy (containing also ^{13}C) contaminant molecules in the residual phase. The isotope value in the hotspot was measured -33.1 ‰ for dichlorprop (data not shown) and the $\delta^{13}C_{4\text{-CPP}}$ minimum was -31.2 ‰. Both dichlorprop and 4-CPP racemic mixtures were in very high concentrations, indicating low/no degradation in the hotspot. On the contrary, the difference between their isotope values (-1.9 ‰) indicated an ongoing 4-CPP degradation. Moreover, $\delta^{13}C_{4\text{-CPP}}$ became 4 ‰ less negative along the groundwater flow, indicating degradation also outside the hotspot (Figure 8c). 4-CPP concentrations were low in the western pathway in samples rich with heavier isotopes. This interesting trend can be explained by physical limitation of substrate bioavailability in clay till or back diffusion of non-degraded 4-CPP from clay matrix, as reported for chlorinated solvents at other sites (e.g. Hunkeler et al., 1999; Morrill et al., 2005; Morrill et al., 2009; Song et al., 2002).

Enantiomer and isotope analysis can be combined if enantiomer forms are measured for isotope values separately. $\delta^{13}C_{dichlorprop}$ was measured to be -35.6 ‰ in both enantiomer forms (data not shown), confirming the assumption that this value is the initial one. $\delta^{13}C_{4\text{-CPP}}$ differed considerably between the two enantiomer forms in the hotspot. The left enantiomer had less negative values (Figure 8d), confirming that 4-CPP is degraded in the hotspot as indicated by the combined metabolite and isotope analysis. Added value of combined enantiomer and isotope analysis in the hotspot is that it characterizes the degradation as (S)-preferable. $\delta^{13}C_{4\text{-CPP}}$ fractionates stronger (gets less negative) in (S)-4-CPP within the hotspot and close to it (difference between (R) and (S) is negative), whereas (R)-4-CPP fractionates stronger close to the stream (the difference is positive). The differences in fractionation of the (R) and (S) forms of 4-CPP indicate an alteration of the degradation under less reduced conditions in the western pathway, as also reported in the studies of Harrison et al. (2003) and Williams et al. (2003). Combined isotope and enantiomer analysis gave a more detailed insight in the anaerobic degradation of phenoxy acids. This study showed the dependence of degradation on changes of redox conditions in field, which was beyond the reach of analyses on metabolites and redox parameters in several field campaigns.

3.2.2 Fate of phenoxy acids in aerobic conditions

The fate of phenoxy acids in the aerobic part of the site was investigated by degradation indicators measurement in groundwater samples from a seepage meter (Milosevic et al., **III**) and by aerobic batch experiments on sediment sampled next to the seepage meter (Batioglu-Pazarbasi et al., **IV**). Enantiomer excess values measured in the seepage meter (13 %) and in the upgradient wells (7-23 %) overlapped, not indicating any alteration of the degradation mechanism in the hyporheic zone (Figure 8b). However, higher $\delta^{13}C_{4\text{-CPP}}$ in the seepage meter than in the upgradient wells indicates 4-CPP degradation in the discharge zone. Combined enantiomer and isotope approach revealed alteration from (S)- to (R)-preferable degradation of 4-CPP in the discharge zone.

Aerobic batch experiment of dichlorprop degradation in the sediment of the hyporheic zone showed high degradation (substrate mineralization) potential, calculated as fraction of ^{14}C-labelled CO_2 compared to of ^{14}C-labelled substrate (Figure 9).

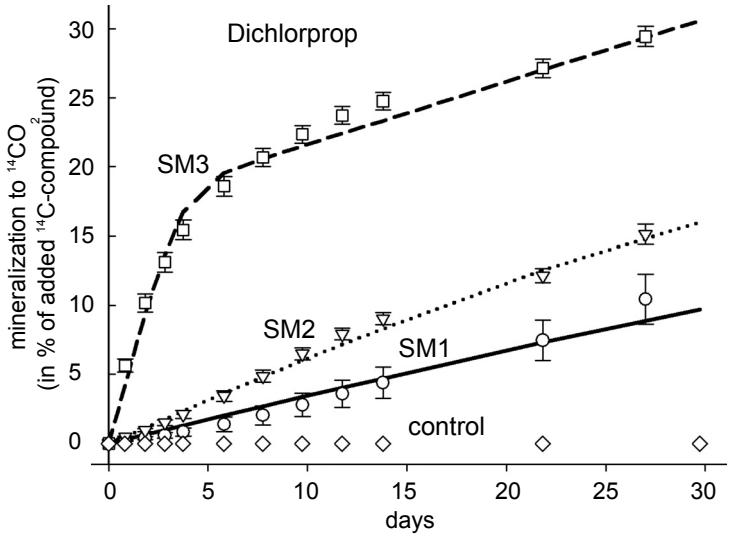

Figure 9: Aerobic mineralization of dichlorprop in microcosm sampled on three locations with different soil structures along the Risby Stream. Degradation potential is high in the hyporheic zone, modified after Batioglu-Pazarbasi et al. (**IV**).

The hyporheic zone was confirmed as a place of attenuation of xenobiotic compounds. Cell abundance and gene diversity of the specific degrader communities were measured, expressed in terms of targeted 16S rRNA gene copy numbers estimated from DNA and quantity of the specific catabolic gene, respectively. Assumed that the aerobic fractionation rates for dichlorprop and 4-CPP are similar, dichlorprop fractionation can be related to the indicators of

4-CPP degradation. The degradation is ongoing in the aerobic part of the contaminant flow path, but it is not expected to considerably decrease the 4-CPP mass discharge into the stream since the ecologic conditions in the stream are poor. The hyporheic zone is thin (5-15 cm of the top streambed) as a result of a regular (once a year) dredging of the stream and high sedimentation of fine particles. The hyporheic zone is therefore probably not the most important place of contaminant attenuation but it can have potential in case it gets broader (30-50 cm) e.g. by stream restoration measures.

3.2.3 Impact of phenoxy acids on the stream

4-CPP was the only phenoxy acid detected in the aerobic Risby Stream. Its temporal variation was, similarly to leachate indicators, not as high in groundwater as in the stream. It ranged from below the detection limit in rainy seasons to the groundwater ranges (50-80 µg/L) in the standing stream water in dry seasons (Figure 10). However, its yearly discharge from highly permeable sand layers of clay till into the stream was ~10 mg/y, which is considered low (Argese et al., 2005). Additionally, 4-CPP gets attenuated below the detection limit less than 1 km from the landfill down the Risby Stream. Therefore ecologic risk probably lies during the periods of dry summers when 4-CPP accumulates in the standing stream water. For instance, aquatic plants and animals in the reproduction stage can be drastically affected on locations where leachate-affected groundwater discharges into the stream.

Ecotoxicity of 4-CPP is rather unknown but 8,000-9,000 µg/L is estimated as the approximate acute toxicity level (EC50) for dichlorprop (Argese et al., 2005). Even lower 4-CPP concentrations are expected to exert synergistic effects in mixtures (Borgmann and Borgmann, 1997; Roy and Bickerton, 2012), especially with other phenoxy acids or persistent inorganics in landfill leachate with proven toxic effects such as ammonium (Kjeldsen et al., 2002). Ammonium in the Risby Stream reached lethal concentrations (>~4 mg/L) for most aquatic organisms (Clement et al., 1996). However, ecologic risk was outside the scope of this research and the ecotoxic effect of 4-CPP was not assessed.

The highest chemical impact was surprisingly located outside the discharge area. It was in the peat area of the former wetland, 100 m downstream the landfill, indicating that surface runoff, local drainage pipes or prolonged back diffusion of leachate from peat streambed can be important discharge routes. The importance

of surface runoff for chemical impact on a local stream was already shown at other landfill sites (Douglass and Borden, 1992; Yusof et al., 2009).

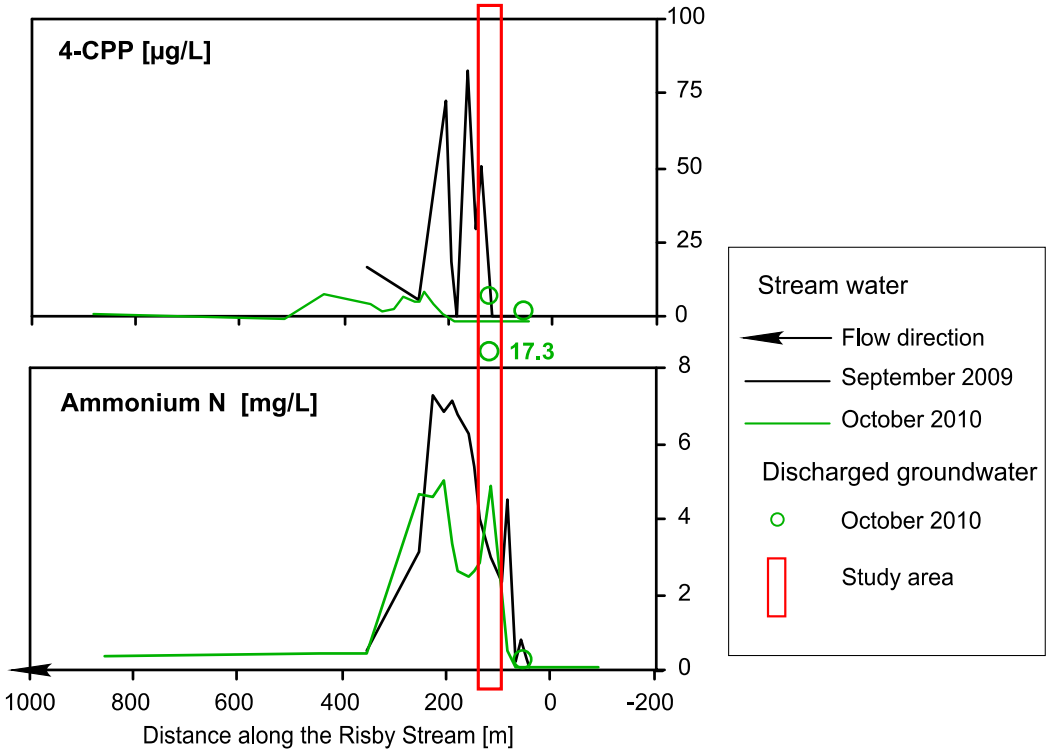

Figure 10: Chemical impact of landfill leachate on the Risby Stream measured at middle stream flow in October 2010 and at zero stream flow in September 2009. Impact is the highest in the peat area ~100 m downstream the studied clay till area, modified after Milosevic et al. (**II**).

3.3 Fate of chlorinated solvents

The entire sequence of chlorinated solvents (Figure 5) was detected consistently only in the hotspot of the Risby Landfill, dominated by cDCE and VC were predominant (Milosevic et al., **II**). Concentrations in clay till outside the hotspot were under the detection limit already within a distance of 15 m. This result agrees with the immobilization of BTEX compounds at a site with clay geology reported by Van Stempvoort et al. (2007).

Chlorinated solvents are not prone to enantioselective analysis but they constitute a sequence of metabolites of reductive dechlorination which enables their grouped fate assessment. Minimal isotope values of each compound and the isotope values of initial contaminants can be assessed using the modelling approach of Hunkeler et al. (2002) where degradation (dechlorination) and isotope fractionation are coupled. Milosevic et al. (**III**) iteratively estimated first order degradation kinetics. The study used the smallest isotope fractionation rates

and expected initial isotope values from the literature (Meckenstock et al., 2004; Shouakar-Stash et al., 2003). PCE and TCE were assessed as the original pollutants and their degradation to vinyl chloride was confirmed using the model. The model proves favourable environmental conditions for dechlorination and indicates back release of contaminants from clay matrix. Both processes might apply also to phenoxy acids, since phenoxy acids are also chlorinated compounds and they also might stay isolated and non-degraded in the clay matrix.

3.4 Fate of BTEX

Fate of BTEX compounds (Figure 11) was not assessed using the same method for chlorinated solvents since the compounds have independent degradation pathways – they do not form a sequence. Isotope values of BTEX in the hotspot were measured within the expected ranges for industrial products (Harrington et al., 1999) and the degradation *in situ* could not be verified. However, a qualitative estimation of anaerobic degradation was made by Milosevic et al. (**III**) based on the differences in BTEX isotope signatures in the hotspot of pollution. High concentrations and low isotope values indicated BTEX degradation. Petroleum derivatives were immobilized in high concentrations within the hotspot as reported at another site in clay settings (Van Stempvoort et al., 2007). BTEX compounds consist merely ~2.5 % of DOC concentration in the hotspot (Milosevic et al., **II**), but bearing in mind their ongoing degradation, they can be a potential electron donor in dechlorination of chlorinated solvents or even phenoxy acids.

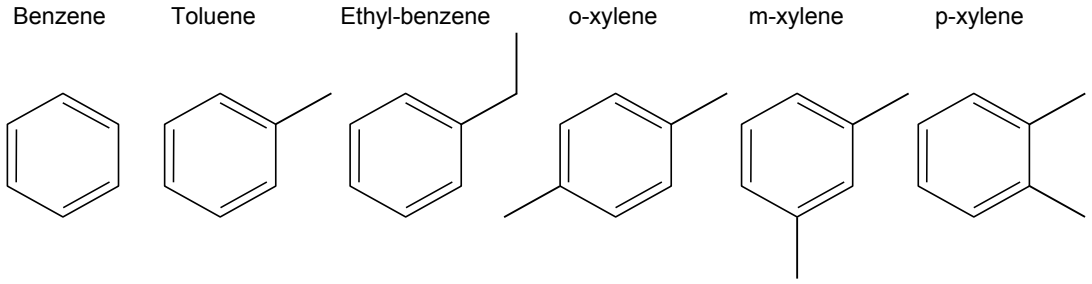

Figure 11: Structural formulas of petroleum derivatives: benzene, toluene, ethylbenzene, ortho-, meta- and para-xylene (BTEX)

3.5 Evaluation of fate assessment methods

Numerous fate studies were done on anaerobic landfill leachate (Table 3), mostly in homogeneous sandy/gravel aquifers. On the contrary, not many field studies were done in complex settings with low permeability geologic units due to

technical complexity and high costs (Christensen et al., 2001). The central fate assessment method of Milosevic et al. (**III**) in complex settings at the Risby Landfill was CSIA. Metabolite and enantiomer analyses were added for the fate of phenoxy acids and metabolite data was coupled in the model for chlorinated solvents. BTEX was assessed only by isotope analysis.
CSIA of mixed contaminants contributed to distinguishing of the contamination hotspots, which was initially based on analysis of leachate indicators. Application of CSIA along the groundwater flow was possible for phenoxy acids, revealing changes of degradation mechanism at low substrate concentrations. Transformation of dichlorprop to 4-CPP was also indicated. However, a shortcoming of isotope analysis usage without supportive microbial studies was reflected in the inability to quantify the degradation. On the one hand, CSIA is not efficient when contaminants can not be tracked along the groundwater flow. We experienced this with immobilized contaminants that might sorb to clay – chlorinated solvents, BTEX and possibly dichlorprop. Their isotope values could not be expressed as a function of the distance between the hotspot and the point of compliance i.e. of the time needed for the contaminant to travel that distance. On the other hand, fractionation rates are usually not available in literature for complex or not frequently used contaminants such as phenoxy acids, which prevents their quantification along the groundwater flow. No laboratory study on aerobic or anaerobic isotope fractionation of dichlorprop or 4-CPP has been reported so far.

Derivation of the degradation rates from compound-specific fractionation rates should be done with precaution when applying CSIA in environmental conditions (Blessing et al., 2009). It should be kept in mind that all fractionation rates are obtained under laboratory conditions and such interpolations can always be a source of uncertainty.

Benzyl succinic acid is a metabolite of toluene, ethyl-benzene and xylene, and can be used as a degradation indicator in their fate assessment (e.g. Baun et al., 2003). However, benzyl succinic acid was not analyzed at the Risby Landfill.

The use of multiple methods for fate assessment revealed heterogeneity of waste deposition and differences in anaerobic attenuation within ~10 m distances. They are complementing each other and since the concentration-based methods are less expensive to perform than CSIA, they were used first in the early steps of the field study.

4. Conclusions

The knowledge about the attenuation of landfill leachate contaminants at heterogeneous geologic settings has been deepened in this study. Anaerobic degradation of selected phenoxy acids, chlorinated solvents and BTEX was shown based on their isotope, metabolite and enantiomer analysis. Concepts, tools and technologies for investigation of water quality are improved for the characterization of poorly studied ground- and surface waters related to clay till impacted by landfill leachate.

Driven wells enabled identification of confined groundwater pathways in clay till. Moreover, temperature measurements of the streambed in cold and warm season revealed the exact locations of groundwater discharge zones in clay till.

Groundwater discharge into the Risby Stream was quantified in a downscaling manner. First a box model of landfill groundwater budget was built for estimation of discharge into the stream. The discharge zones in clay till were identified and the discharge was calculated for these zones. Hydraulic potentials were measured by piezometers placed in sand lenses of clay till and provided maximal values of groundwater discharge into the local stream. Seepage meters provided the quantification of minimal discharge values.

Contaminant mass discharge was calculated from the discharge zone area in clay till, groundwater discharge quantified by seepage meters and contaminant concentrations measured in seepage meter samples. The contaminant mass discharge was compared with the intrinsic mass discharge of the stream. The contribution from groundwater was regarded as a gauge of chemical impact on the stream and the impact was quantified for mobile inorganic and organic landfill leachate contaminants. The values mostly depended on seasonal hydrologic changes of the stream, and the highest impact was estimated in peat sediments downstream the clay till area.

Fate of phenoxy acids was quantified by tracking their isotope and enantiomer fractionation along the groundwater flow. Well–known isotope fractionation rates of chlorinated solvents were combined with metabolite ratios as the second degradation indicator. It was sufficient for identification of the initial contaminant compounds, bottlenecks of the biodegradation and a back-diffusion of non-degraded contaminant phase. BTEX degradation was indicated by isotope values.

CSIA was the main method for indication of natural attenuation without supportive microcosm experiments, but fractionation of phenoxy acids along the flow and well-known fractionation values for chlorinated solvents and BTEX were used instead. Usage of solely indirect methods for assessment of natural attenuation is less certain than the complete approach including microcosms, but it can speed up management of numerous landfill (or generally contaminated) sites and disturbed ground- and surface waters.

Groundwater-surface water transition zone is indicated as a place of enhanced attenuation of landfill leachate-originating contaminants. A wider hyporheic zone i.e. a hyporheic zone in more natural conditions might have a regulation function in the attenuation of the xenobiotic landfill leachate contaminants that impact the Risby Stream.

5. Perspectives

The work carried out in this study revealed research directions for further explanation of the fate of landfill leachate-originating xenobiotic compounds at complex geologic settings.

Some of the applied hydrogeologic and chemical methods for the conceptual model formulation have an outlook for further development.

- Confined groundwater pathways within the sand lenses of clay till impacted by organic landfill leachate were preliminarily identified by **geophysical measurement and subsequent mathematical inversions** of obtained signals (Fiandaca et al, 2012). The locations identified by driven wells were supported by the findings of combined geophysical and mathematical approach. These findings may possibly lead to development of the new method for landfill leachate identification in clay till.

- Vertical contaminant transport facilitated by fractures of clay till has been studied in the field scale (e.g. McKay et al., 1999), but **transport in sand lenses** is still uncertain (McKay et al., 1998). A finer vertical discretization of groundwater flow and contaminant concentration within the sand lenses might improve the hydrogeologic site model. Concentration maxima in the middle or in the bottom of the confined pathway were observed on the Risby Landfill (data not shown). A more detailed tracer study (e.g. isotopes or conservative compound concentration) may be done from the hotspot to the downgradient points of compliance for quantification of the **dilution in the sand lenses below the landfill**. Improved understanding of the sand lenses' hydrogeology in the conceptual model would enable an **upgrade to numerical groundwater flow model**.

- Contaminant mass discharge from peat has not been quantified although maximum chemical impact on the stream was measured in peat area of the Risby Landfill. **Contamination pathways through peat** should be taken into account in future contaminant fate assessment at old landfill sites, since many of such sites are located in former wetlands (Lorah et al., 2009).

There are additional methods or sampling strategies suitable for fate assessment of organic contaminants in clay till.

- Hyporheic zone was the most challenging for the study due to its high dynamics in hydrology, chemistry and microbial structure and activity. The usage of **passive samplers** might overcome the problem of seasonal variations of these parameters and interpolations of the results. For instance, diffusive gradients in thin-film (DGT) can be used for stuck soil pollution sorbed to sediments, DOC and colloids (Garofalo et al., 2004), whereas contaminant trap on silicone can mimic biodegradation *in situ* (Mayer et al., 2011). Big advantage of passive samplers is their possibility to assess chemical availability and accessibility of substrate for microorganisms, which can be further related to toxicity and chemical activity of the target compounds. The disadvantage is, similarly to CSIA, that the methods are not always optimized for more complex contaminants.

- Usage of **multilevel samplers** (Rivet et al., 2008a) would improve the characterization of the hyporheic zone and calculation of groundwater discharge. It would provide high-resolution depth profiles of the streambed and delineation of groundwater-stream water mixing zones. It would also support the assessment of contaminant mass discharge, contaminant degradation and chemical impact on the stream.

- Apart from a microcosm study on enrichment factors which lacked for the Risby Landfill, measurement of concentrations and isotope signatures of **BTEX metabolites** (benzyl succinic acid and benzoic acid) would enable combined metabolite and isotope fate assessment similarly to chlorinated solvents.

Finalizing of the model using microbial methods can be improved through a better assessment of environmental stressors that can impact microorganisms.

- Among all complicating factors in fate assessment using microbial methods (Bombach et al., 2010), **suppressors of microbial growth** are relatively simple for analysis, which would be a quick indicator for eventual lack of degradation of e.g. phenoxy acids in the mixture of landfill contaminants in the hotspot. Antibiotics, biocides, additives to petroleum derivatives, anti-

freezing agents and other suppressors of anaerobic microbial growth were not analyzed at the Risby Landfill.

Final outlooks concern general ecological aspect of the study.

- High spreading of 4-CPP stresses out the relevance of **ecotoxicological studies on metabolites and transformation products, especially in mixtures** with the parent compounds and usual inorganic compounds such as ammonium.

- The only case of high landfill leachate impact on the stream was shown for a two-month long period without precipitation (Milosevic et al., **II**). Therefore, **climate change phenomena** have to be taken into consideration in assessment of chemical impact from point-sources of pollution such as the Risby Landfill, particularly in respect with the foreseen longer and drier summers. Climate change-mitigating measures for restoration of natural stream habitats (e.g. meander building) would enhance development of the hyporheic zone and microbial attenuation in the zone, and decrease the impact of landfill leachate on the stream.

- Chemical impact and degradation processes estimated for phenoxy acids can be integrated into an **ecological impact assessment tool** similar to the tools for chlorinated solvents and BTEX by e.g. Haarstad and Borch (2008). McKnight et al. (2012) proposed a choice of specific methods for the assessment of chemical impact from point-sources of pesticides on local stream ecosystems, but landfill leachate pesticides have never been put into an ecological perspective.

- McKnight et al. (2012) indicated that the release of pesticides bound on stream sediment or surface runoff particles is highly important for seasonal deteriorating of good ecological status of the investigated streams. It is similar to the highest chemical impact on the Risby Stream in the wetland, where peat-rich sediments probably back-released the landfill leachate contaminants. Particle-related contamination, such as back-sorption, potentially has the central role for stream ecosystem status. Therefore, further research on the **interplay between the particle structure and chemical dynamics of leachate contaminants** would improve the assessment of particle-related chemical impact on the stream. Even though mid-stream sampling sufficed

for detection of places of the highest chemical impact, Martin et al. (1992) showed the importance of cross sectional integrated sampling strategy for estimation of particle-related contamination.

- Temperature measurements in various sediment types (Milosevic et al., **II**) can be a basis for modeling groundwater discharge into the surface water over longer stream stretches. **Chemical/ecological impact on the catchment area** can be based on such calculation of groundwater i.e. contaminant mass discharge

- Concepts, tools and technologies for investigation of ground- and surface waters in clay till impacted by landfill leachate can be applied for **integrative water quality assessment.** Such integrative assessment of all water bodies is set as a goal of EU Water Framework Directive (European Commission, 2000).

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7. Papers

I Thomsen, N.I., Milosevic, N. and Bjerg, P.L., 2012. Application of a mass balance method at an old landfill to assess the impact on surrounding water resources, submitted manuscript

II Milosevic, N., Thomsen, N.I., R.K. Juhler, Albrechtsen, H.-J. and Bjerg, P.L., 2012. Identification of discharge zones and quantification of contaminant fluxes into a local stream from a landfill in heterogeneous geological settings, Journal of Hydrology, DOI 10.1016/j.jhydrol.2012.04.012, in press.

III Milosevic, N., Qiu, S., Elsner, M., Einsiedl, F., Albrechtsen, H.-J. and Bjerg, P.L., 2012. Combined isotope and enantiomer analysis to assess the fate of phenoxy acids in a heterogeneous geologic setting at an old landfill, manuscript in preparation

IV Batioglu-Pazarbasi, M., Milosevic, N., Malaguerra, F., Binning, P.J., Albrechtsen, H.-J., Bjerg, P.L. and Aamand, J., 2012. Discharge of landfill leachate to streambed sediments impacts the mineralization potential of phenoxy acid herbicides depending on the *tfdA* gene diversity, manuscript in preparation

The papers are not included in this web-version, but can be obtained from the Library at DTU Environment. Contact library@env.dtu.dk or Department of Environmental Engineering, Technical University of Denmark, Miljoevej, Building 113, DK-2800 Kgs. Lyngby, Denmark.

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